Available online at www.sciencedirect.com

SciVerse ScienceDirect

Physics Procedia 44 (2013) 114 – 119

Physics Procedia

10th International Conference on Solid State Chemistry, Pardubice, Czech Republic

# Study of $As_{50}Se_{50}$ thin film dissolution kinetics in amine based solutions

Pálka K.[a]*, Vlček M.[a], Kovalskiy A.[b]

[a] *Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, Czech Republic*
[b] *Department of Physics and Astronomy, Austin Peay State University, Clarksville, Tennessee, U.S.A.*

**Abstract**

Chalcogenide glass thin films are suitable materials for micro optical elements fabrication due to their convenient physical and chemical properties. They are generally photosensitive and thus can be selectively etched. Therefore they can be exploited as photoresists in photolithography. In this paper we deal with the study of $As_{50}Se_{50}$ thin films dissolution kinetics in EDA based solutions. The detailed evolution of the etching curves is discussed and the dependences of the average etching rate on the composition and temperature of the etching bath are described.


Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.

*Keywords:* chalcogenide thin film; etching; $As_{50}Se_{50}$

## 1. Introduction

Chalcogenide glasses have been intensively studied for their promising physical and chemical properties since their discovery in 1950's. Because of the substitution of oxygen atom in the glass structure by chalcogen atom(s) – sulfur, selenium or tellurium – the properties of these glasses significantly differ from oxide glasses. By introducing larger and heavier atoms into the glass matrix values of the refractive index increase up to 2 - 3.2, the temperature of the glass transition decreases and optical transmission in infrared spectral region is significantly extended (up to 20 μm). It is known that many chalcogenide glasses exhibit considerable photosensitivity [1]. This phenomenon is usually much more significant if chalcogenide glasses are in thin film form and it is dependent on the thin film preparation method.

The high refractive index, IR transmittance and photosensitivity make chalcogenide glasses very promising materials in practical applications especially in optics. Besides macroscopic optical elements (such as lenses for IR spectral range) chalcogenide glasses can be used as micro (nano) optical elements

* Karel Pálka. Tel.: +420-466-037-252 ; fax: +420-466-037-068.
*E-mail address*: karel.palka@elits.cz.


Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.
doi:10.1016/j.phpro.2013.04.015

such as diffraction gratings, micro lens arrays, beam splitters, couplers etc. These diffractive optical elements (DOE) can be effectively fabricated in chalcogenide glasses due to photoinduced changes in their chemical reactivity which results in selective etching rates of exposed and un-exposed parts of the sample [2]. The depth of structural changes in the sample of given composition is determined by the wavelength of the light beam. Usually thin films are exposed to an electromagnetic beam with energy equal or higher than the optical band gap of the sample and the exposure is done either through the mask containing the desired structure [3] or the pattern can be "written" into the sample by holography technique [4] or using a focused laser beam scanning over the surface as well [5], respectively.

It is important to know the kinetics of the dissolution process for exposed and un-exposed parts of thin film in order to obtain the desired etched structures of the highest possible quality. To achieve highly selective etching it is necessary to understand which factors influence significantly kinetics of the dissolution. Thus this paper deals with influence of concentration of the etching agent in the etching solution, temperature of the etching process and rate of the bath's flow on the etching kinetics of un-exposed (i.e. virgin) samples. Influence of the exposure on the kinetics of the etching process will be published elsewhere.

## 2. Experimental

Source bulk material was prepared by melt quenching method using high purity arsenic and selenium. Thin films were prepared using vacuum thermal evaporation method (Tesla Corporation, model UP-858). Thickness of thin films was 1000 nm. Solutions of ethylenediamine (EDA) in aprotic solvent were chosen as the etching baths. EDA concentrations varied from 0.1 to 0.7 $mol.l^{-1}$. Solutions were kept at 25, 30, 35, 40 and 45°C and stirred by peristaltic pump at a rate of 26 $ml.min^{-1}$. The volume of the etching solution used per experiment was 18 ml. The size of the samples submersed into the etching solutions was approximately 11x19 mm. Transmission spectra of thin films during the etching process were recorded by modular spectrometer (StellarNet Inc.). Each time record was evaluated at six wavelengths corresponding to three maxima and three minima in low-absorbing part of film's transmission spectra.

## 3. Results and discussion

The homogeneity of freshly prepared thin film's dissolution rate within the entire thickness was expected. This presumption can be expressed by a straight line with fixed point at coordinates $t = 0$ s and $d_{REL} = 100$ (relative remaining thickness of thin film in range 0-100) in the plot of the etching curve. Fig.1 gives evidence that real progress of dissolution rate of non-exposed thin films is close to the linear model. Nevertheless, systematic deviations apart from this linear model were observed.

In order to highlight these deviations the etching curves were differentiated. If the linear model is valid, the time dependence of the etching curve's derivative should be constant. The typical shape of the differentiated etching curve is given in Fig.2. It is apparent that the etching rate in the first part of the etching process increased until a limit value of the etching rate is achieved. From this point the etching rate decreases. The time $t_{REL}$, where the rate of the etching process reaches the maximal value (relative to the time needed to complete dissolution of the thin film), varied with EDA concentrations and temperatures of the experiments. With increasing concentration of EDA in the etching solution the values of $t_{REL}$ increased as well.

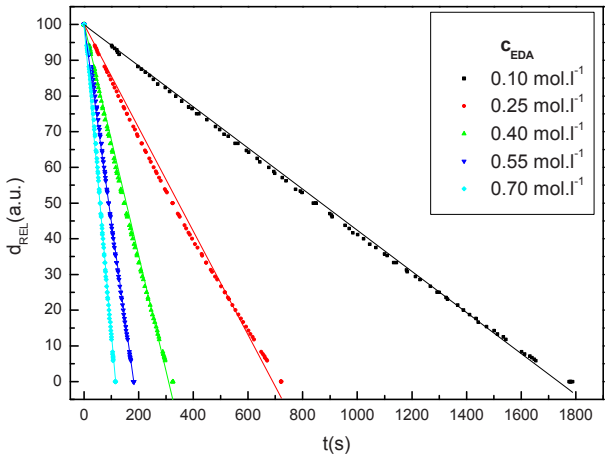


Fig.1. The etching curves with fitted lines for the $As_{50}Se_{50}$ thin film samples etched at 25°C in EDA solutions of various concentrations.

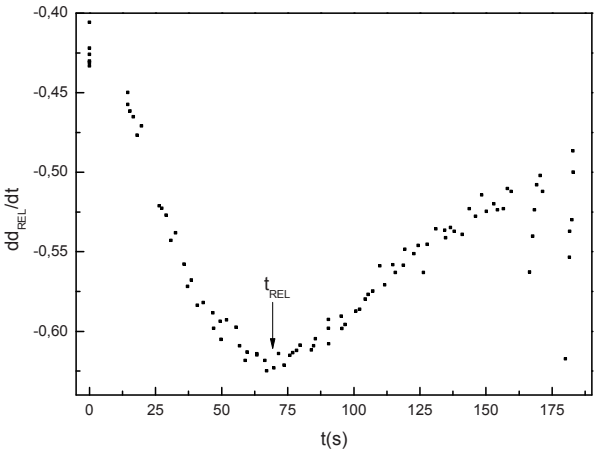


Fig.2. The derived etching curve ($c_{EDA}$ = 0.55 mol.l$^{-1}$; 25°C) for the $As_{50}Se_{50}$ thin film sample etched in EDA solution.

Explanation of these phenomena can be found in two separate processes. The first one responsible for the increase of the etching rate is self-catalytic effect [6]. Products of the chemical reaction between etching solution and the surface of the thin film increase the rate of further etching process. The second phenomenon influencing the progress of the etching rate is establishing chemical equilibrium. As the thin film is being etched off, the concentration of EDA in the etching solution decreases. With decreasing concentration of EDA the probability of successful chemical interaction of EDA and the surface of the thin film decreases. Thus the rate of the thin film's dissolution slowed down.

In order to verify the presence of the self-catalytic effect a series of experiments with different rate of the etching bath's flow were done. Fig.3 gives evidence that with decreasing rate of the etching bath's flow (and thus higher concentration of the etching products near the thin film's surface) the etching rate significantly increases and full dissolution of film is achieved in shorter time.

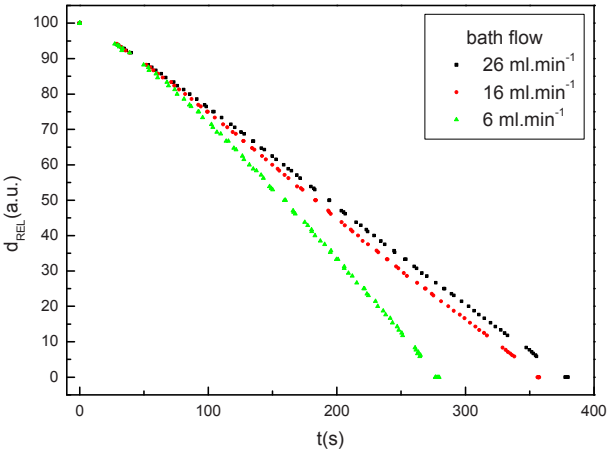


Fig.3. Dependences of etching kinetics on the rate of the bath's flow for the $As_{50}Se_{50}$ thin film samples etched at 25°C in EDA solution.

The depletion of the etching agent (EDA) in the etching solution as the phenomenon responsible for the decrease in the etching rate can be proven by dependence of $t_{REL}$ on the EDA concentration in the etching solutions (for constant temperature) (Fig.4). With increasing concentration of EDA in the etching solutions the values of $t_{REL}$ increases as well. Because the depletion of EDA by dissolving the thin film is constant, the decrease in its concentration influences the etching rate less thus the change of the etching rate's tendency occurs later in the etching process.

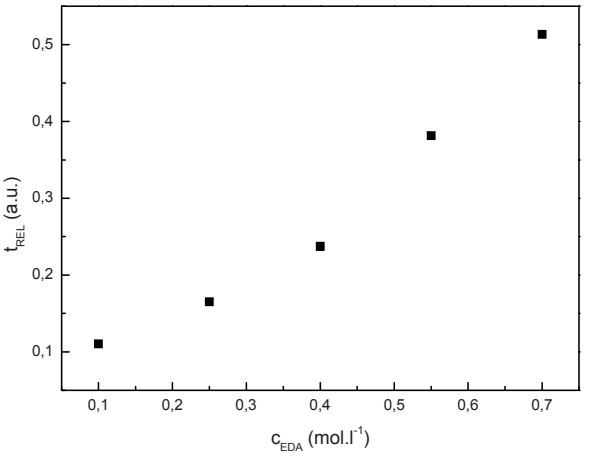


Fig.4. Dependence of $t_{REL}$ on the concentration of EDA in the etching solution (25°C) for the $As_{50}Se_{50}$ thin film samples.

Even if the rate of the etching process is not perfectly constant, its fluctuations are nearly negligible for high rates of the etching bath's flow. In this case the etching kinetic can be expressed by straight line with fixed point at coordinates t = 0 s and $d_{REL}$ = 100. The absolute values of the slopes of these fitted lines represent average etching rates constant for the entire etching process. These average rate parameters were used to study the dependences of the etching rate on EDA concentration in the etching solution and the temperature of etching. All the etching rates increased with increasing temperature of etching process and with increasing concentration of EDA, as shown in Fig.5.

The activation energy of the etching process can be calculated from temperature dependence of the etching rate using Arrhenius' equation [7]:

$$v = A \cdot e^{-\frac{E_a}{RT}} \quad (1),$$

where $v$ is the etching rate, $A$ stands for the frequency factor, $E_a$ is the activation energy, $R$ is the universal gas constant and $T$ is the temperature of the experiment. The average activation energy $E_a$ = 55.5 kJ.mol$^{-1}$ was deducted from data in Fig.5. The activation energy of the etching process was not concentration dependent since the slopes of curves in Fig.5 are nearly identical.

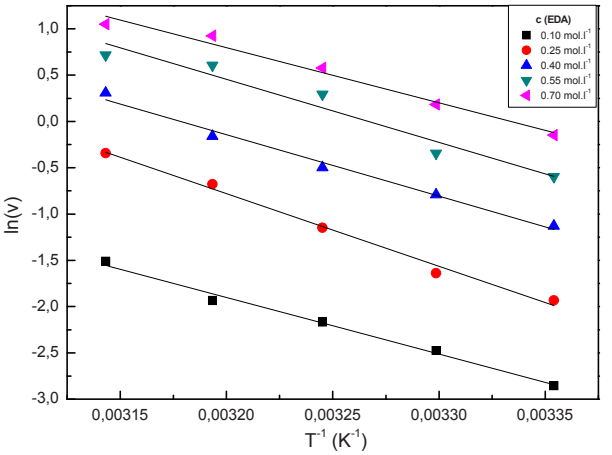


Fig.5. Temperature dependences of etching rates (ln(v)) for the $As_{50}Se_{50}$ thin film samples etched in EDA solutions of various concentrations.

## 4. Conclusion

The kinetics of $As_{50}Se_{50}$ thin films dissolution in EDA based solutions has been studied. It was found that the depth dependence of the etching rate of un-exposed thin films is nearly linear. Deviations from the linear progress were caused by self catalytic effect (increase of the etching rate) and by depletion of etching agent in the etching bath (decrease of the etching rate). The deviations caused by self-catalytic effect can be avoided or reduced by an increase in etching bath's flow. The deviations caused by the depletion of the etching agent occurred at higher etching times for higher concentrations of EDA in the etching solutions.

For higher rates of the etching bath's flow the etching curve can be substituted by a fitted straight line with fixed point at coordinates t = 0 s and $d_{REL}$ = 100. The slope of this fitted line expresses the average etching rate constant for the whole etching process. The activation energy of $As_{50}Se_{50}$ thin film dissolution in EDA based solutions was calculated from the temperature dependences of the average etching rates using the Arrhenius equation resulting in the average value of $E_a$ = 55.5 kJ.mol$^{-1}$.

## Acknowledgements

This work was financially supported by the grant P204/11/0832 from the Czech Science Foundation.

## References

[1] Přibylová H, Antoine K, Vlček M, Jain H. Kinetics of laser-induced photodarkening in arsenic based chalcogenide glasses. *Thin Solid Films* 2011;**519**: 3950-3953

[2] Kovalskiy A, Vlček M, Jain H, Fišerová A, Waits CM, Dubey M. Development of chalcogenide glass photoresists for gray scale lithography. *J Non-Cryst Solids* 2006;**352**,:589-594

[3] Eisenberg NP, Manevich M, Noach S, Klebanov M, Lyubin V. New types of microlens arrays for the IR based on inorganic chalcogenide photoresists. *Mater Sci Semicond Process* 2000;**3**:443-448

[4] Teteris J, Reinfelde M. Holographic recording in amorphous chalcogenide semiconductor thin films. *J Non-Cryst Solids* 2003;**326–327**: 494-499

[5] Schroeter S, Vlček M, Poehlmann R, Fišerová A. Efficient diffractive optical elements in chalcogenide glass layers fabricated by direct DUV laser writing. *J Phys Chem Solids* 2007;**68**:916-919

[6] Zenkin SA, Mamedov SB, Mikhailov MD, Turkina EYu, Yusupov IYu. Mechanism for interaction of amine solutions with monolithic glasses and amorphous films in the As-S system. *Glass Phys Chem* 1997;**23**:393-399

[7] Vlček M, Frumar M, Kubový M, Nevšímalová V. The influence of the composition of the layers and of the inorganic solvents on photoinduced dissolution of As-S amorphous thin films. *J Non-Cryst Solids* 1991;**137-138**:1035-1038